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Development of an electrochemical sensor for potassium ions based on $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ modified electrode

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Abstract

In the work described by this paper, we studied the development of a selective potassium ion sensor constituted of a carbon paste electrode modified (CPEM) with a novel $\text{KSr}_2\text{Nb}_2\text{O}_{15}$. The material $\text{KSr}_2\text{Nb}_2\text{O}_{15}$ is an oxide with the tetragonal tungsten bronze structure (TTB) type are in forefront both in the area of research as well as in industrial applications. The sensor response to potassium ions was linear in the concentration range 1.26×10^{-5} at 1.62×10^{-3} mol L^{-1} ($E \text{ (mV)} = 32.7 + 51.1 \log [\text{K}^+]$). The sensor based $\text{KSr}_2\text{Nb}_2\text{O}_{15}$, of the TTB-type presented very good potentiometric response, with a slope of 51.1 mV/dec (at 25 °C) and detection limit for the potassium ions of $7.27 \times 10^{-5} \text{ mol.L}^{-1}$.

Keywords: potassium ion sensor, tetragonal tungsten bronze structure, potentiometric detection

1. Introduction

Potassium monitoring in serum, urine, and foods is very important in the clinical and medical fields, being one of the most important routine analysis performed in a clinical laboratory. From the potassium determination, medical information concerning physical conditions of the patients can be obtained in the cases where renal diseases, hypopotassemia, alkalosis, cirrhosis of liver, diuretic drugs, etc. are suspected. On the other hand, when the potassium concentration in human serum becomes higher than 9 mmol L^{-1} , the heart often stops [1]. Hence, accurate, easy and rapid sensing of potassium ions is very important.

The oxides with the tetragonal tungsten bronze structure (TTB) type are in forefront both in the area of research as well as in industrial applications. Taking into account TTB structure type, a wide variety of cations substitution is possible due the presence of several interstices in the structure [2]. The construction and potentiometric evaluation of a novel $\text{KSr}_2\text{Nb}_2\text{O}_{15}$ based carbon paste electrode as potassium ion sensor was investigated.

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2. Experimental

Precursor of the $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ powder was prepared by the mechanical mixture of oxides via high energy ball milling method, as described elsewhere [2]. Thus, the material was dried at 373 K in a grove box. The one was calcined in a furnace of type tube with oxygen atmosphere. The heating cycle was carried out via two calcination steps with major one at 1423 K being maintained during 10 hours. The powder obtained was characterized by X-ray diffraction (XRD). A diffractometer with Cu- $\text{K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) and a graphite monochromator were used.

The sensor was prepared by carefully mixing 55% (m/m) of graphite powder, 25% (m/m) $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ powder and 20% (m/m) of mineral oil. The modified carbon paste was packed into an electrode body, consisting of a plastic cylindrical tube (surface area of 12.6 mm^2) equipped with a stainless steel staff serving as an external electric contact.

Cyclic voltammetric and potentiometric measurements were carried out with an μ -Autolab type III (Eco Chimie) controlled by a personal computer. The cyclic voltammetric measurements were performed in a three-electrode cell using a carbon paste electrode modified (CPEM) with $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ as a working electrode (indicator electrode), saturated calomel electrode (SCE) as reference and platinum auxiliary electrode. The potential range was from -0.55 to +0.3 V (vs. SCE) at scan rate of 5 mV s^{-1} , and during the measurements the solution in the cell was not flowed. The potential differences between the indicator sensor (CPEM) and reference electrodes were measured using the GPES software (Eco Chimie) by chronopotentiometry (zero current).

3. Results and discussion

3.1. Characterization of $\text{KSr}_2\text{Nb}_5\text{O}_{15}$

Measurements were carried in the angular range $5^\circ \leq 2\theta \leq 120^\circ$, the scanning step of 0.02° and fixed counting time of 30 s. X-ray diffraction analysis showed only the set of diffraction lines of a lattice with tetragonal symmetry and noncentric space group $P4bm$ (100) [2], corresponding to one listed in the JCPDS card number 34-0108. The diffraction pattern was refined in according to the Rietveld method. The refinement was performed using the program Fullprof [3]. From crystallographic parameters as relative occupancies, atomic coordinations (x, y, z), lattice parameters and space group, the tridimensional representation of unitary cellule was constructed, using the CaRIne Crystallography 3.1® software, as shown in Figure 1. From determination of sites present in the structure of the $\text{KSr}_2\text{Nb}_5\text{O}_{15}$, all pentagonal (A) sites are occupied by equal quantity of Sr^{2+} and K^+ and all tetragonal (B) sites are occupied only Sr^{2+} ions. Otherwise, the trigonal (C) sites are empty. It is due to the strontium (Sr^{2+}) and potassium (K^+) ionic ray values, which are sufficiently large to block that its occupy the C site. The development of sites in the $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ can be associated to the formation of NbO_6 octahedral arrangement.

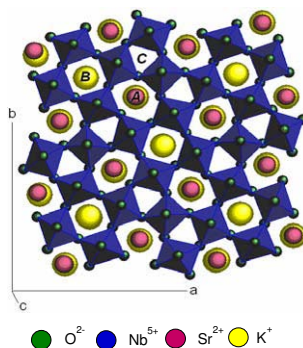
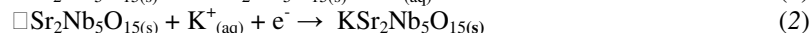
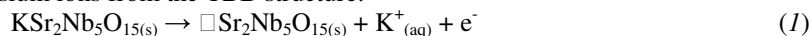


Fig. 1. Representation of sites in the Tetragonal Tungsten Bronze (TTB) structure of the $\text{KSr}_2\text{Nb}_5\text{O}_{15}$.

3.2. Electrochemical behavior of the sensor

First, the voltammetric behavior of the sensor in TRIS buffer solution (pH 8.3) containing 0.5 mol L^{-1} potassium ions was investigated. The cyclic voltammograms obtained with the CPEM (Figure 2) presented one peak on both anodic (peak I: -0.04 V) and cathodic (peak II: -0.37 V vs. SCE). This electrochemical activity is due to the extraction topotactic process of the potassium ions from the TBB structure:



where \square is vacant site.

From the linear relationship i_p vs. scan rate^{1/2}, it can be seen that the redox reaction is controlled by the diffusion process of potassium ions in TBB structure. In the absence of potassium ions, no voltammetric response was observed for the CPEM with $\text{KSr}_2\text{Nb}_5\text{O}_{15}$, confirming that the response of the sensor is a function of the insertion reaction of potassium ions in the structure. It is necessary to emphasize that before taking the potentiometric measurements, the modified electrode needs to be submitted by cyclic voltammetry in solution containing potassium, because without this treatment was not observed a satisfactory response.

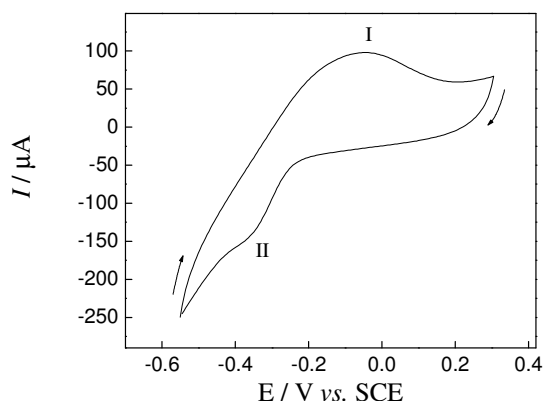


Fig. 2. Cyclic voltammogram for 0.5 mol L^{-1} potassium ions in 0.1 mol L^{-1} Tris buffer solution at the sensor based $\text{KSr}_2\text{Nb}_5\text{O}_{15}$. $\nu = 5 \text{ mV s}^{-1}$.

3.3. Potentiometric behavior of the sensor

Using the parameters optimized as described above for the carbon paste electrode modified with $\text{KSr}_2\text{Nb}_5\text{O}_{15}$, the analytical curve was constructed by injecting different concentrations of potassium ions solutions between 5.50×10^{-5} and $1.60 \times 10^{-3} \text{ mol L}^{-1}$ (Fig. 3).

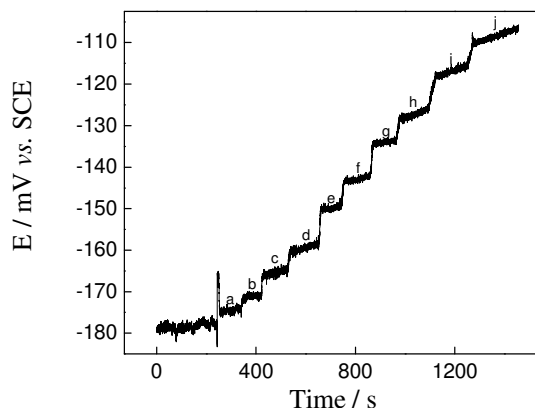


Fig. 3. Transient potentiometric signals obtained in for ten reference solutions of potassium ions. (a) 5.5×10^{-5} ; (b) 7.9×10^{-5} ; (c) 1.3×10^{-4} ; (d) 1.8×10^{-4} ; (e) 3.0×10^{-4} ; (f) 4.1×10^{-4} ; (g) 6.4×10^{-4} ; (h) 8.5×10^{-4} ; (i) 1.3×10^{-3} and (j) $1.6 \times 10^{-3} \text{ mol L}^{-1}$. Stirring rate = 300 rpm.

Figure 4 show the potentiometric response of the sensor in function of the logarithm of potassium ions concentration in solution. A linear region is observed in the interval of potassium concentration between 1.26×10^{-5} at $1.62 \times 10^{-3} \text{ mol L}^{-1}$ ($E \text{ (mV)} = 32.7 + 51.1 \log [\text{K}^+]$). The sensor based $\text{KSr}_2\text{Nb}_2\text{O}_{15}$, of the TTB-type presented very good potentiometric response, with a slope of 51.1 mV/dec (at 25 °C) and detection limit for the potassium ions of $7.27 \times 10^{-5} \text{ mol.L}^{-1}$.

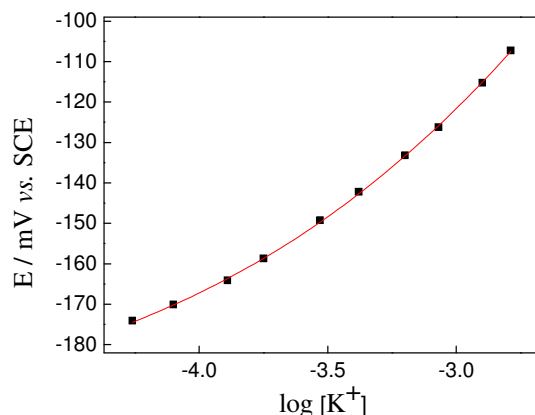


Fig. 2. Equilibrium potentials of potentiometric potassium sensor for different potassium concentrations.

4. Conclusion

The $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ shows strong promise for potential application as a potentiometric sensor for potassium ions. The mechanism of the sensor depends on the electrochemical activity of the $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ with extraction/insertion topotactic processes of the potassium ions from the tetragonal tungsten bronze structure. The potential of the sensor are linearly proportional to potassium ion concentration in the range 1.26×10^{-5} to $1.62 \times 10^{-3} \text{ mol L}^{-1}$ with a correlation coefficient of 0.9997. The lifetime of the sensor was approximately six months.

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